drochloride) was filtered off. The filtrate was washed with water and dried with $MgSO_4$, and after the ether had been driven off the residue was distilled in vacuum in the presence of pyrogallol (polymerization inhibitor). Information on the substances obtained is given in the table.

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3 July 1967

Institute of Organic Chemistry AS ArmSSR, Erevan

REACTIONS OF 1,5-DIKETONES

II. Reaction of Methylenedicyclohexanone and Tricyclohexanolone with Ammonium Acetate in Acetic Acid*

V. I. Vysotskii and M. N. Tilichenko

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 4, pp. 751--752, 1969

UDC 547.835.2

The Chichibabin pyridine synthesis with methylenedicyclohexanone and tricyclohexanolone has been studied. It has been shown that under the conditions of the synthesis tricyclohexanolone is previously isomerized into methylenedicyclohexanone. The reaction products are sym-octahydroacridine, 12-hydroxy-Δ^{10}-dodecahydroacridine, and 5-azabicyclo[8,4,0]tetradecane-6,11-dione. The latter two substances are the products of the conversion of the Δ^{10}-dodecahydroacridine that arises as an intermediate.

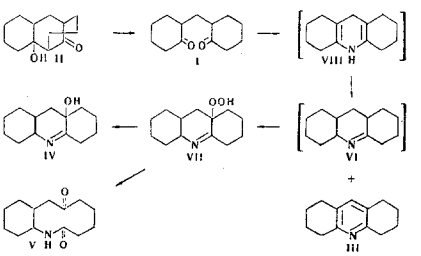
The initial products of the reaction of ammonium acetate with carbonyl compounds in acetic acid (the improved Chichibabin (Tschitschibabin) pyridine synthesis [2]) are, obviously, dihydropyridines. During the reaction they either disproportionate to form a mixture of pyridine and piperidine bases [3] or are oxidized to pyridines [2]. In the 1,5-diketone series the Chichibabin pyridine synthesis has so far been studied inadequately. It is known only [4] that some methylenedicyclanones give 2,3:5,6-dicyclanopyridines under these conditions.

We have carried out this reaction with 2,2'-methylenedicyclohexanone (I) and the product of its intramolecular ketolization—tricyclohexanolone (II). In both cases, sym-octahydroacridine (III)—the main reaction product—, 12-hydroxy-Δ^{10}-dodecahydroacridine (IV), and 5-azabicyclo[8,4,0]tetradecane-6,11-dione (V) were isolated.

The identity of the results in the two cases indicates that tricyclohexanolone first isomerizes under the reaction conditions and then reacts as the diketone I. A similar decyclization process has been observed previously for 4-phenyl- and 4-furyltricyclohexanolones [5].

The formation of compounds IV and V becomes clear if it is assumed that in the process Δ^{10}-dodecahydroacridine (VI) is formed as an intermediate. It has been shown previously [6] that VI is oxidized in the air to 12-hydroperoxy-Δ^{10}-dodecahydroacridine (VII), which is subsequently reduced to 12-hydroxy-Δ^{10}-dodecahydroacridine or rearranges to form the macrocyclic ketolactam V. We have confirmed this hypothesis with the diketone I or the ketol II in an atmosphere of argon. When the reaction product obtained was oxidized with oxygen in heptane we obtained the hydroperoxide VII, identical with that obtained from authentic Δ^{10}-dodecahydroacridine (VI).

Compounds III and VI are apparently formed by the disproportionation of the decahydroacridine VIII produced initially:



EXPERIMENTAL

A mixture of 16.0 g (~0.08 mole) of the methylenedicyclohexanone I or the ketol II, 16.0 g (~0.2 mole) of ammonium acetate, and

*For part I, see [1].

65 ml (~1.0 mole) of acetic acid was boiled for 2 hr, cooled, made alkaline, and extracted with benzene. The benzene extracts were dried with magnesium sulfate, the benzene was driven off, and the mixture was distilled in vacuum. In the range from 150 to 160° C (6 mm) 10.0 g of a distillate crystallizing during distillation was collected.

1.4 g of the distillate was triturated with 10 ml of petroleum ether. The insoluble fraction was filtered off and the filtrate was evaporated, giving 1.1 g of a crystalline mass with mp 69° C (from hexane) forming a picrate with mp 199–200° C (from ethanol). The substances obtained melted without depression in admixture with authentic samples of sym-octahydroacridine and its picrate. The fraction insoluble in petroleum ether (0.2 g) was washed repeatedly with boiling water and the residue was recrystallized from ethanol, mp 191–192° C. It gave no depression of the melting point with an authentic sample of 12-hydroxy-Δ^{10}-dodecahydroacridine (IV). The aqueous extracts were evaporated to dryness. The residue (about 0.1 g) had 157–158° C (from acetone or dioxane) and gave no depression of the mp with an authentic sample of 5-azabicyclo[8,4,0]tetradecane-6,11-dione (V).

The reaction in an atmosphere of argon was carried out similarly and with the same amounts of substances. After heating for 2 hr, the mixture was made alkaline and extracted with benzene, the benzene extract was dried with magnesium sulfate, the benzene was driven off, and the residue was distilled in vacuum. The operations of drying, eliminating the benzene, and vacuum distillation were also carried out in an atmosphere of argon. 11.7 g of distillate was collected in the range from 120–135° C (0.2 mm). It consisted of a viscous liquid partially crystallizing on standing in a sealed vessel.

A solution of 1.55 g of the distillate in 10 ml of heptane was oxidized with molecular oxygen. In 2 hr, 58 ml of O_2 was absorbed, 38 ml of this having been absorbed in the first 10 min. The precipitate of hydroperoxide that had deposited was filtered off and dried at 0° C over paraffin wax, giving 0.5 g of the hydroperoxide of Δ^{10}-dodecahydroacridine (VII), mp 96° C, showing no depression on fusion with an authentic sample. After the removal of the hydroperoxide, the filtrate was evaporated to dryness, giving 0.9 g of sym-octahydroacridine (III), mp 69° C (from hexane).

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3 July 1967

Far Eastern State University, Vladivostok

ELECTRONIC INTERACTION BETWEEN THE NITROGEN, OXYGEN, AND SILICON ATOMS IN THE MOLECULES OF α-AZIRIDIN-1-YLALKOXY(TRIETHYL)SILANES

V. A. Pestunovich, M. G. Voronkov, V. N. Perchenko, Yu. Yu. Popel, L. G. Batalova, and N. S. Nametkin

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 4, pp. 753–755, 1969

UDC 546.287

By the PMR method we have established the existence of a high frequency of the inversion of the nitrogen atom in the molecules of α-aziridin-1-ylalkoxysilanes. This is due to the fact that the high (because of $p_\pi - d_\pi$ bonding with the silicon atom) electronegativity of the oxygen atom in the Si–O–C–N system makes possible an interaction between the unshared electron pair of the nitrogen atom and the antibonding orbital of the C–O bond. The latter, in its turn, increases the degree of $p_\pi - d_\pi$ bonding between the oxygen and silicon atoms (in these compounds the order of the Si–O bond is greater than in the alkoxysilanes).

The α-aziridin-1-ylalkoxy(triethyl)silanes (I and II) which we were the first to study by the PMR method are, at the present time, the only synthetically accessible class of aminoalkoxysilanes containing a nitrogen atom in the α position with respect to the oxygen atom.

It might have been expected that in the molecules of these compounds the electronic interaction between the silicon, oxygen, and nitrogen atoms would have an extremely peculiar nature because of the possibility of the delocalization of the unshared electron pair of the nitrogen on the antibonding orbital of the C—O bond.

A similar interaction in the N—C—X system has recently been considered within the framework of the MO LCAO theory [1, 2]. It was found that in this system the interaction should be enhanced to a considerable extent by an increase in the electronegativity of the X-atom. Furthermore, the delocalization of the unshared pair of electrons of the nitrogen atom on the antibonding orbital of the C—X bond is facilitated with a planar arrangement of the valence bonds of the N-atom. This is due to the fact that the orbital of the unshared pair of the nitrogen is closer to the 2p type, facilitating its maximum overlapping with the corresponding orbital of the C—X bond.